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## A method for coating carbon nanotubes with titanium

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**Abstract:** The surfaces of acid-functionalized carbon nanotubes (CNTs) were coated by TiO<sub>2</sub> produced by the hydrolysis of TiCl<sub>4</sub>, which was converted into Ti through temperature-programmed reduction (TPR) equipment. SEM, TEM, XRD, and EDAX analyses were used to characterize the primary CNTs, as-prepared TiO<sub>2</sub>-coated CNTs and the Ti-coated CNTs. It was found that after the functionalization of CNTs by ultrasonic-assisted acid treatment, TiO<sub>2</sub> was successfully coated onto the CNTs, which was reduced in TPR under H<sub>2</sub>/Ar flow at 850 °C to metal Ti. The Ti transition layer is important for the formation of composites of CNTs with other metals.

**Keywords:** Coating; Nanocomposite; Carbon nanotubes; Titanium

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### 1 Introduction

With the development of micro- and nano science in the past few decades, a lot of research has been done as is reflected in the huge number of papers published and patents filed. Since 1991, when carbon nanotubes were discovered by Iijima<sup>[1-3]</sup>, comprehensive studies have been performed for the application of the precious mechanical and electrical properties of this material in various industries<sup>[1, 4-5]</sup>.

Multiwalled carbon nanotubes (MWCNTs) are more appropriate as a template for metal-oxide coatings compared with single-walled carbon nanotubes (SWCNTs) not only because of their lower cost, but also because of their higher concentration of the probable functional groups after functionalization<sup>[6]</sup>. Generally, a composite of porous carbon with Titania (TiO<sub>2</sub>) photocatalysts could potentially combine the adsorption effects by pores with photodegradation effect of TiO<sub>2</sub> to increase the removal of light sensitive chemical dyes and pollutants. TiO<sub>2</sub> is one of the most studied semiconductors for various applications ever since Fujishima and Honda<sup>[7]</sup> reported the electrochemical photolysis of water using this material<sup>[8]</sup>. Moreover, MWCNTs could be considered an appropriate support for materials with field-emission displays and photocatalytic properties. Thus, a combination of TiO<sub>2</sub> and MCWNTs could potentially create

many active sites for photocatalytic degradation<sup>[9-11]</sup>. In this work, a CNT/TiO<sub>2</sub> dioxide nanocomposite was processed to finally produce Ti-coated CNTs.

With regard to the inert property of CNTs, it is necessary to add functional groups on the CNT surface in order to enable them to take part in reactions. This makes it possible to produce metallic, ceramic, and polymeric-based composites and also to carry out coating on the CNTs with ceramic materials such as silica and metallic materials such as Au, Pd, Fe, Ag<sup>[12-15]</sup>, and nanogold bunches<sup>[16-17]</sup>.

In principle, the nanowires of any metal can be obtained in a similar manner by simply depositing metal onto the CNTs if the formation of a homogeneous coating on CNTs is realized. This is true only for a limited number of metals, including Ti, that have strong interactions with CNTs<sup>[14]</sup>, as it has already been cited<sup>[18-19]</sup>. Many types of metals do not form continuous structures on the CNT surface because of a weak metal-carbon interaction<sup>[14]</sup>. Therefore, in this study, Ti was selected to be finally coated on the CNTs.

As is evident in the literatures<sup>[20-22]</sup>, the sol-gel coating is considered the most commonly adopted method that introduces an inorganic phase onto the CNT substrate<sup>[23-24]</sup> compared with many reported methods, especially for CNT/TiO<sub>2</sub> nanocomposites such as several chemical methods<sup>[25]</sup>, chemical and

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physical vapor depositions<sup>[26-27]</sup>, hydrothermal and solvothermal syntheses<sup>[28-30]</sup>, sonochemical processing<sup>[31]</sup>, and electrospinning<sup>[32]</sup>.

Indeed, researchers have paid a great deal of attention to the synthesis of CNT/TiO<sub>2</sub> nanocomposites. For example, Chen et al.<sup>[33]</sup>, Wang et al.<sup>[34-35]</sup>, and Jitianu et al.<sup>[36]</sup> used a modified sol-gel method to prepare them using different precursors. An et al.<sup>[37]</sup> deposited anatase TiO<sub>2</sub> onto CNTs via the hydrolysis of titanium isopropoxide in supercritical ethanol. Song et al.<sup>[38]</sup> studied the effect of heat treatment on the performance of TiO<sub>2</sub>-Pt/ MWCNT catalysts for methanol electro-oxidation. Pang et al.<sup>[39]</sup> showed that Pt nanoparticle-decorated CNT/TiO<sub>2</sub> electrodes remarkably improved catalytic activities for the oxidation of hydrogen peroxide. Kuo et al.<sup>[40]</sup> synthesized CNT-grafted TiO<sub>2</sub> as an electrically conductive catalyst for the oxidation of NO gas under electrical excitation, apart from UV irradiation. Yu et al.<sup>[41]</sup> studied the synthesis of TiO<sub>2</sub>-MWCNT hetero-junction arrays on the Ti substrate with a controllable thickness of the TiO<sub>2</sub> layer for the photodegradation of phenol. Akhavan et al.<sup>[42]</sup> reported the synthesis of aligned MWCNT arrays coated by a thin TiO<sub>2</sub> layer. Generally, the most fundamental route for the creation of carbon-TiO<sub>2</sub> nanomaterials involves simple mixing. This is usually performed in a solution and, possibly, with the pre-functionalization of surfaces<sup>[43]</sup>. This may be done in order to acquire a good dispersion, especially if water is used as a solvent (carbonaceous nanomaterials are hydrophobic), and/or to enhance the adsorbance of TiO<sub>2</sub> or its reactants<sup>[43-44]</sup>. One of the simplest methods of the carbon doping of TiO<sub>2</sub> nanomaterials is by direct oxidation of the Ti metal in the flame of a burner<sup>[45-47]</sup>. Hydrothermal synthesis<sup>[48]</sup> is also employed, and it involves a reaction under a controlled temperature and/or pressure. The solvothermal method is almost identical, with the exception that the solvent used is non-aqueous, thus allowing higher temperatures to be achieved<sup>[43]</sup>. Deposition techniques are also utilized, which include physical vapor deposition (PVD), chemical vapor deposition (CVD), and electrophoretic deposition (EPD)<sup>[49]</sup>. The most common synthesis routes and precursors used across the range of nanocarbon-TiO<sub>2</sub> photocatalysts are summarized in Table 1<sup>[43]</sup>.

As mentioned earlier, the sol-gel technique is the most widely applied method in which either intimate mixing or chemical interactions between the carbon nanomaterial and TiO<sub>2</sub> are achieved<sup>[50]</sup>. Despite many studies carried out by other researchers on the sol-gel method, this research involves a promising simple sol-

gel like technique that prepares CNT/TiO<sub>2</sub> nanocomposites with the overall aim of producing Ti-coated CNTs. The reasonable results have led our research team to decide on the further development of this technique for upcoming works. However, in this study, a modified colloidal method was utilized.

**Table 1 Common nanocarbon-TiO<sub>2</sub> synthesis techniques and precursors<sup>[43]</sup>**

Method	Common precursors
Simple mixing	TiO <sub>2</sub>
	Carbon nanomaterial
Thermal oxidation	Ti metal
	Titanium carbide
Sol-gel	Metal alkoxides, (R-O-)4Ti
	Titanium isopropoxide
	Titanium isobutoxide
	Titanium ethoxide
	Titanium tetrachloride Titanium oxysulphate
Hydrothermal	Titanium tetrachloride
	Titanium sulphate
	Titanium isopropoxide
PVD	Ti metal
	TiO <sub>2</sub>
CVD	Titanium isopropoxide
	Titanium isobutoxide
EPD	TiO <sub>2</sub>
	Carbon nanomaterial

## 2 Experimental

### 2.1 Materials

CNTs (purity > 95%, O. D. = 30-40 nm) was supplied by the Research Institute of Petroleum Industry (RIPI). Titanium tetrachloride (purity > 98%), nitric and sulphuric acid, hydrochloric acid (40 mass% HCl), ethanol, and polyethylene imine (PEI) were purchased from Merck and used without further purification.

### 2.2 Synthesis of complexes

TiO<sub>2</sub> nanoparticles were successfully deposited onto functionalized CNTs via a simple chemical route based on the dissolved TiCl<sub>4</sub> precursor in acid.

#### 2.2.1 Functionalization of CNTs

CNT functionalization treatment was carried out using a mixture of nitric acid/sulfuric acid (1:3 V/V) in an ultrasonic bath (Sel Ultrasons- H model) at 30 °C for 2 h. Samples were subsequently rinsed in distilled water and finally dried in a vacuum oven at 120 °C.

#### 2.2.2 Synthesis of TiO<sub>2</sub> suspension

A suspension of TiO<sub>2</sub> was obtained by following these two steps:

In the first step, a mixture of hydrochloric acid

(40 mass% HCl), distilled water, and  $\text{TiCl}_4$  in a volume ratio of  $\text{TiCl}_4:\text{HCl}:\text{H}_2\text{O} = 30:3:67$  was prepared, and  $\text{TiCl}_4$  was gradually added to the solution. A large quantity of HCl fumes and milky white  $\text{TiO}_2$  suspension were obtained during this step.

In the second step, 1 ml of as-prepared suspension was added to 30 ml of distilled water and a 0.15 mL solution consisting of  $5 \times 10^{-5}$  polyethylene imine. A white precipitate began to appear after 40 min at  $70^\circ\text{C}$ .

### 2.2.3 Synthesis of CNT/ $\text{TiO}_2$ nanocomposite

A solution containing 10 mg of functionalized CNTs was added to the  $\text{TiO}_2$  suspension, stirred at  $70^\circ\text{C}$ , centrifuged (4500 r/min), and washed in distilled water to remove the remaining acid. Subsequently, the drying step was performed at  $80^\circ\text{C}$  for 24 h to obtain the composite powder.

## 2.3 Physical measurements

### 2.3.1 X-ray crystallography

The X-ray diffraction (XRD) patterns were recorded using a PW130 Phillips diffractometer with graphite monochromated  $\text{Cu } K\alpha$  radiation in the  $10\text{--}70^\circ$  ( $2\theta$ ) angular, which was employed to study the phase of the CNTs,  $\text{TiO}_2$ , and CNT/ $\text{TiO}_2$  nanocomposites.

### 2.3.2 Scanning electron microscopy (SEM)

SEM and energy dispersive analysis by the X-ray (EDAX) model JEOL-6700 F were employed to study the microstructure and determine the percentage of the elements in the nanocomposites.

### 2.3.3 Transmission electron microscopy (TEM)

TEM model JEM-100CX $\alpha$  was utilized to study the microstructure.

### 2.3.4 Temperature-programmed reduction (TPR)

TPR In order to determine the reduction conditions, equipment (TPR, Micromeritics 2900) was employed. A gas containing 1.5%  $\text{H}_2$  in an Ar environment with a rate of 50 SmL/min (SmL, mL at standard condition, i. e. at  $0^\circ\text{C}$  and 100 kPa)<sup>[20]</sup> for 90 min and a heating rate of  $10^\circ\text{C}/\text{min}$  until  $850^\circ\text{C}$  was conducted into the equipment loaded with 0.056 mg of the CNT/ $\text{TiO}_2$  nanocomposite. The  $\text{TiO}_2$  was converted to Ti in the reduction reactor at the reduction conditions.

## 3 Results and discussion

### 3.1 SEM and TEM images of primary CNTs

Figs. 1 and 2 depict, respectively, the SEM and TEM images of the primary CNTs containing SWCNTs and MWCNTs.

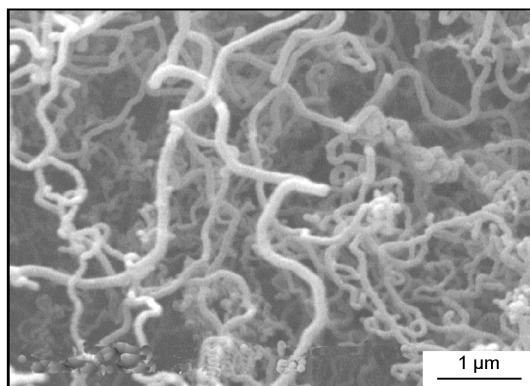


Fig. 1 SEM image of the primary CNTs

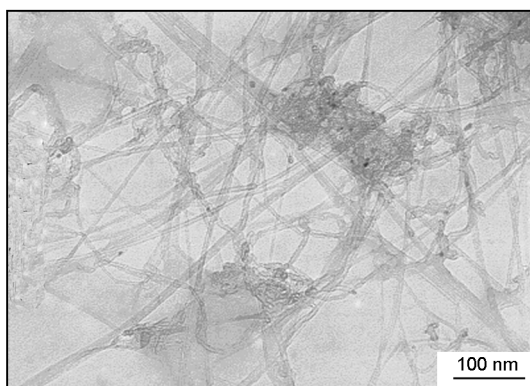


Fig. 2 TEM image of the primary CNTs

### 3.2 Functionalization of CNTs

With regard to the inert behavior of the CNTs and taking them part in reactions, it is necessary to introduce some functional groups<sup>[51]</sup> on the CNT surfaces. MWCNTs have defects, atomic vacancies, and slip planes. Although an ideal graphene layer is chemically inert, the surface can be functionalized from the defect sites at the surfaces and the chemically reactive centers for the  $\text{TiO}_2$  nano-coating<sup>[6]</sup>.

In the presence of strong acids and ultrasonic forces, some of the available bonds on the surface of the CNTs were broken, and carboxyl acids ( $-\text{COOH}$ ) and hydroxides ( $-\text{OH}$ ) were introduced<sup>[2]</sup>, which improved the dispersion of the CNTs in the mixture and prevented deposition with increasing time. After the functionalization, primary CNTs and functionalized ones were rinsed in water. It is obvious that the former were floated or deposited, whereas the latter were almost homogeneously dispersed. Weak bonds between the functional groups of the dispersed CNTs and the polar molecules of water resulted in dispersion, which is not very stable.

### 3.3 Formation of nano TiO<sub>2</sub> particles on CNTs

Various Ti compounds have been applied by other researchers as starting materials to produce TiO<sub>2</sub> nanoparticles such as TiCl<sub>4</sub><sup>[52]</sup>, TiF<sub>4</sub><sup>[22]</sup>, alkoxide precursors such as Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> dissolved in ethanol<sup>[53]</sup> or in isopropanol<sup>[9]</sup>, titanium (IV), and n-butoxide (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti). However, in this study, an acidic mixture containing TiCl<sub>4</sub> was prepared to be used in TiO<sub>2</sub> nanoparticle production.

As stated earlier, the chemically inert CNT surfaces should be functionalized for taking part in reactions. Once the functionalization is completed, it should, therefore, be possible to use the functional groups on the CNT surfaces as initiation points for chemical reactions<sup>[6]</sup>.

A complete bonding between the Ti atoms and the oxygen atoms on the surfaces of the TiO<sub>2</sub> nanoparticles forms a saturated TiO<sub>6</sub>, but an incomplete bonding toward the outer surface of the nanoparticles results in an unsaturated TiO<sub>x</sub> (TiO<sub>x</sub> is an unsaturated compound) ( $x < 2$ ). With regard to the presence of

functional groups, for example, —COOH and —OH on the functionalized CNTs and also the unsaturated structures (TiO<sub>x</sub>) among the TiO<sub>2</sub> nanoparticles, the formation of HO<sub>6-x</sub>-Ti-(OTi)<sub>x</sub> or (H<sub>2</sub>O)<sub>6-x</sub>-Ti-(OTi)<sub>x</sub> bonds is indeed expected<sup>[54]</sup> and, as a result, the formation of a TiO<sub>2</sub> layer on the surfaces of the CNTs is realized as well. Figs. 3 and 4 depict, respectively, the SEM and TEM images of the TiO<sub>2</sub> nanoparticles coated on the CNTs.

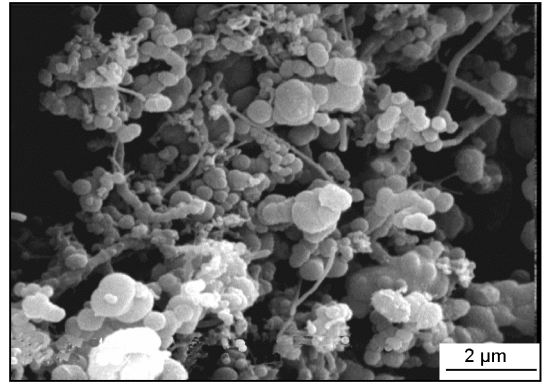


Fig. 3 SEM image of the TiO<sub>2</sub> nanoparticles coated on the CNTs

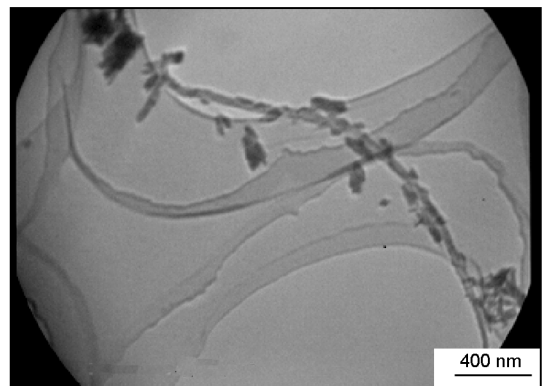
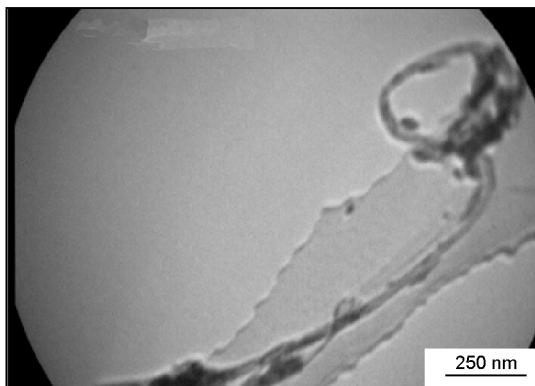
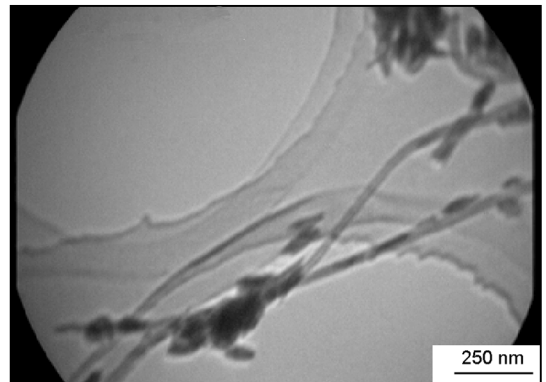
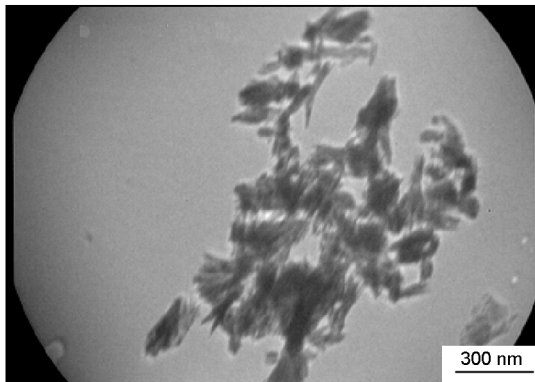


Fig. 4 TEM images of the TiO<sub>2</sub> nanoparticles coated on the CNTs at different magnifications

In addition, XRD pattern of the nanocomposite is depicted in Fig. 5. As can be seen, the anatase, rutile, and brookite phases attributed to TiO<sub>2</sub> and also

carbon are evident.

### 3.4 Temperature-programmed reduction (TPR)

Two diagrams are obtained according to Fig. 6.



Fig. 6a depicts the temperature profile in TPR. Fig. 6b shows the variations in transmission voltages (mV) with time, which indicates that a peak point (B) was reached after 50 min when the reduction reaction (Eq. 1) was complete<sup>[55-56]</sup>.

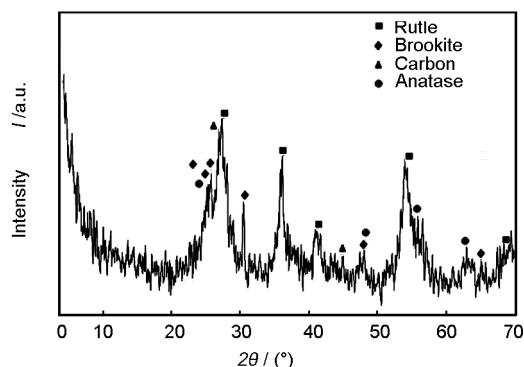
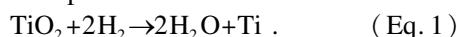


Fig. 5 X-ray diffraction pattern of the  $\text{TiO}_2/\text{CNT}$  nanocomposite

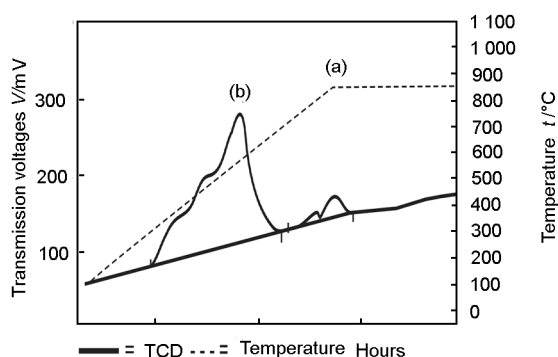


Fig. 6 (a) TPR profile and (b) transmission voltage (mV) variations with time in a thermal conductivity detector, indicative of the completion of reduction at peak point B. In all cases, the reduction was conducted under 5%  $\text{H}_2/\text{Ar}$  at a heating rate of  $10^\circ\text{C}/\text{min}$

### 3.5 SEM, EDAX, and XRD analyses

In this research, the surfaces of the acidily functionalized CNTs were coated first by  $\text{TiO}_2$ . As reported in the literature, these nanoscale composites were previously produced using various techniques. For example, in a report by Wang et al.<sup>[57]</sup>, anatase  $\text{TiO}_2$  nanoparticles were covalently anchored onto acid-treated MWCNTs through a nanocoating-hydrothermal process to obtain  $\text{TiO}_2$ -MWCNT nanocomposites. Liu and Zeng<sup>[22]</sup> developed a one-pot chemical approach (in aqueous solution) to prepare mesocrystals of anatase  $\text{TiO}_2$  onto MWCNTs under mild reaction conditions. Meyyappan<sup>[9]</sup> synthesized two kinds of CNT/ $\text{TiO}_2$  composite photocatalysts using an m-Chloroperbenzoic acid (MCPBA) oxidation method, employing MWCNTs and C60 as nanocarbon sources and

TNB (titanium (IV) n-butoxide) as a  $\text{TiO}_2$  source. Gao et al.<sup>[58]</sup> reported a conventional sol-gel method to prepare the CNT/ $\text{TiO}_2$  nanocomposites with different carbon loadings. In this study, after producing the CNT/ $\text{TiO}_2$  nanocomposites, the  $\text{TiO}_2$  nanoparticles were converted into Ti through the TPR equipment by the reduction reaction, as the final step. The SEM images of the Ti-coated CNTs illustrate bead-like and porous coating structures along the CNTs (Fig. 7).

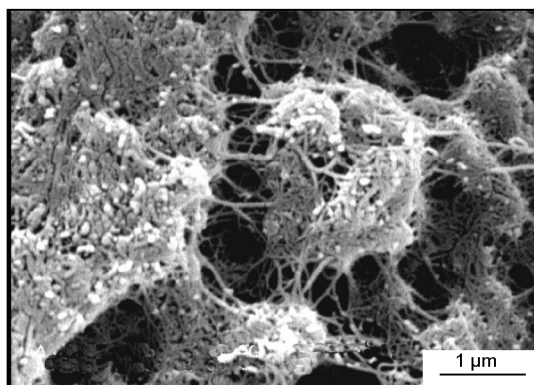


Fig. 7 SEM image of Ti-coated CNTs

These structures can be caused by the decomposition of the  $\text{TiO}_2$  nanoparticles and the emission of oxygen. Moreover, it is obvious from some of the coated parts that the CNTs became bundled. Finally, the composition of the Ti coating on the CNTs was confirmed on the basis of the energy-dispersive analysis by the X-ray (EDAX) and X-ray diffraction (XRD) methods, as depicted in Figs. 8a and 8b, respectively.

The information regarding the O element in the EDAX spectrum has to be taken into account, because it is very important to know whether the  $\text{TiO}_2$  is thoroughly reduced to Ti. As is obvious, the O element could be found at 0.52 keV. However, the existing peak around this range is very small (having extremely low counts on the vertical X-axis). This can confirm the fact that the oxygen amount is negligible if it exists. In addition, the peak about 2.20 keV can be related to the elements Au, Hg, Sr, Zr, or Os; however, with regard to the coating process before the SEM examination, this peak belonged to Au. In addition, the peak about 1.70 keV can be related to the elements Kr, Rb, Y, Tb, Dy, Tm, Hf, or Ta. With regard to the composition of the precursors used, this peak could be related to Y.

It should be mentioned that TiC might be formed at  $850^\circ\text{C}$  at the interface of the CNT and Ti layer. Although the peaks at  $2\theta = 35.99^\circ$  and  $2\theta = 41.80^\circ$  in the XRD spectrum match well with the (111) and

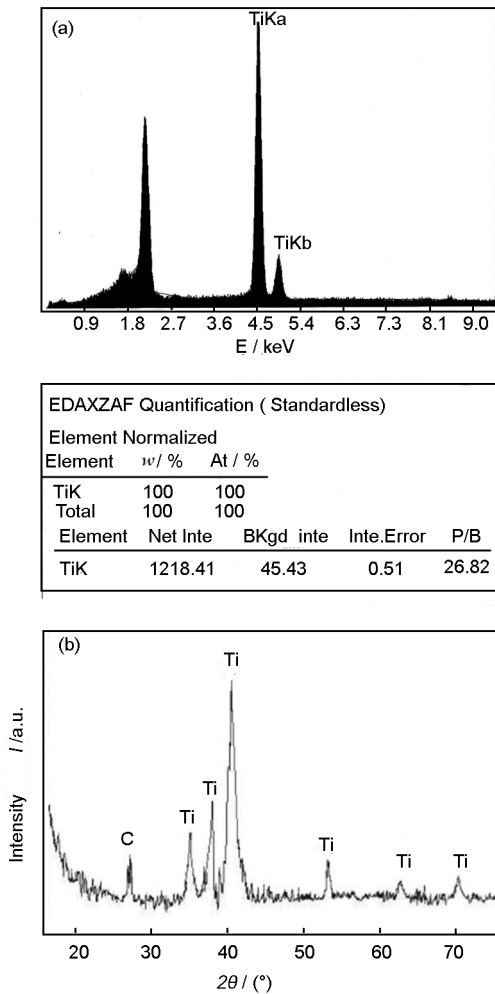


Fig. 8 (a) EDAX analysis and (b) X-ray diffraction pattern of Ti-coated CNTs

(200) crystal planes of TiC, those peaks are very small. Therefore, the TiC amount is really negligible if it exists.

## 4 Conclusions

In the presence of strong acids and ultrasonic forces, some of the available bonds on the surface of the CNTs were broken, and functional groups were introduced, which improved their dispersion in water.

The TiO<sub>2</sub> nanoparticles were produced by the hydrolyses of TiCl<sub>4</sub>, a modified colloidal method (a promising simple sol-gel-like technique), and used for the coating of the CNTs. In the coating process, after mixing the TiO<sub>2</sub> suspension and the functionalized CNTs, a bond between the incomplete surfaces of TiO<sub>2</sub> and the functionalized surfaces of the CNTs was created, and a coating layer of TiO<sub>2</sub> on the CNTs was formed. In order to determine the reduction conditions, TPR equipment was utilized. After achieving

reduction conditions, the TiO<sub>2</sub> was converted to Ti in a reduction reactor, and Ti-coated CNTs were obtained. Since CNTs are chemically inert toward reactions and with regard to achieving strong interactions between CNTs and Ti, the CNT/Ti nanocomposites were chosen to be produced in this research. This obtained nanocomposite would receive special attention if other metals need to be coated on the CNTs with Ti as a transition layer, which could expand the applications of the metal/CNT composites.

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# 碳纳米管表面涂覆钛的新方法

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**摘要:** 采用 TiCl<sub>4</sub> 水解法对表面酸功能化的碳纳米管 (CNTs) 进行 TiO<sub>2</sub> 涂层, 然后通过程序升温还原 (TPR), 使 TiO<sub>2</sub> 涂层转变为 Ti 涂层。利用 SEM、TEM、XRD 和 EDAX 对 CNTs、CNT/TiO<sub>2</sub> 纳米复合材料和 Ti 涂层 CNTs 进行表征。结果表明: 超声波酸功能化 CNTs 后, 可将 TiO<sub>2</sub> 成功地涂覆于 CNTs 表面; 在 850 °C 下、H<sub>2</sub>/Ar 氛围中, 通过 TPR 可将 TiO<sub>2</sub> 涂层还原为金属 Ti 涂层。该 Ti 涂层对 CNTs 和其他金属形成复合材料非常重要。

**关键词:** 涂层; 纳米复合材料; 碳纳米管; 钛

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- ◆ 我司与中南大学、国防科技大学等大中专院校的实验室和研究院合作开发了一系列用于炭材料生产设备, 已经取得了成功的工业规模化生产。主要的设备有: 碳纤维预氧化设备、网带式连续高温炭化炉、真空炭化炉、卧式高温石墨化炉、立式高温石墨化炉、真空CVD/CVI炉和裂解烧成炉等。



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